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A study on improvement over semi-empirical methods using general Joshi – Chhaya model

B A Joshi, V M Chhaya and Smita Chhag
Department of Physics, Saurashtra University, Rajkot-360 005, India

Abstract In favour of precise study of large molecules, semi-empirical LCAO-MO-SCF-CI method is improved by general Joshi-Chhaya model of bi centric repulsion, exchange and hybrid integrals The *ab initio* calculations are impracticable and cumbersome for large molecules Inclusion of mono and bi-centric exchange integrals and truly computed bi centric repulsion integrals is found better to get real picture of spectral properties compared to other methods Pentamerization of HCN to adenine is studied and discussed with highly convincing results of present Joshi-Chhaya model based methods Finally, a problem of strange behaviour of electron-molecular scattering amplitude calculated by highly efficient close coupling method is discussed using present potential surface study of HCN

Keywords Semi-empirical methods, Joshi-Chhaya model, electron-molecule scattering

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1. Introduction

A simple molecule's complicated electronic structure consists of numbers of molecular orbitals which in turn involves a number of atomic orbital contributions. The study using versions of variation method requires various repulsive and attractive potential based integrals which are impracticable to calculate using *ab initio* type, time consuming method. Mostly, the said integral's gross energy changes depend on internuclear distances. ZDO, CNDO, INDO type semi-empirical methods included only repulsion and mono-exchange interactions and the bicentric repulsion was computed wrongly for Rydberg areas. This error was allowed to propagate through whole molecular framework *via* resonance, overlap, exchange, hybrid like repulsion based integrals. As a result, Rydberg excitation, stabilization of MO's, triplet excitation *etc.* obtained were unexpected. In the present paper, encouraging results of various spectral properties are obtained due to truly computed and dominant bi-centric repulsion integrals using Joshi-Chhaya model. Moreover, bicentric exchange integrals (BEI) are formulated using Joshi-Chhaya model and included expecting improvement over S and T excitations. Finally, mono and bi-hybrids are formulated using Joshi-Chhaya and Mulliken approximation and included expecting more stabilization over whole molecular framework. Unfortunately, because

of bifurcations of bi-centric repulsion and exchange integrals according to Rydberg, valence, intra valence, $l = 0 \rightarrow 1, l = 0 \rightarrow 0, l = 1 \rightarrow 1$ *etc.* status, the Pentium computer with 16 M.B. RAM CPU does not response. Inspite of the computer Memory problems some ground state properties calculated by parts are discussed.

2. Formulation

In the present method, only the bicentric repulsion integrals (BRI) are computed truly using Joshi-Chhaya model [1]. Thus, method MRINDO/S is renamed as improved MRINDO/S with proper choice of integer variable 'n' for Rydberg and valence part of the calculation *i.e.* IMRINDO/S - nnn - CI.

As an attempt to study more precisely and to have rational approach for Hartree – Fock energy matrix elements, more and more integrals which were neglected for computation convenience could be retained

The present improved MRINDO/S-nnn including bicentric exchange integrals (BEI) is named as IMRNHI/S-224E-CI. E stands for extrapolation of BRI $nnn = 224$ implies $n = 2$ for valence and intra valence BRI and $n = 4$ for Rydberg BRI. H-F matrix elements of IMRNHI/S-224E-CI are,

$$\underset{\substack{\mu \rightarrow n_1(A) \\ \text{[IMRNHI/S-224E]}}}{F_{\mu\mu}} = \underset{\substack{\mu \rightarrow n_1(A) \\ \text{[MRINDO/S]}}}{F_{\mu\mu}} - \frac{1}{2} \sum_{B \neq A} \left(P_{\mu\mu} \left\langle \mu^B \mu^A / \mu^B \mu^A \right\rangle + \sum_{\nu \neq \mu}^{B} P_{\nu\nu} \left\langle \nu^B \mu^A / \nu^B \mu^A \right\rangle \right).$$

Second term shows the improvement. The different centres BEI $\left\langle \mu^B \mu^A / \mu^B \mu^A \right\rangle$ interact between the atomic orbitals (AO's) with same quantum number (l). $\left\langle \nu^B \mu^A / \nu^B \mu^A \right\rangle$ shows interactions between different centres.

Second term can be simplified as,

$$-\frac{1}{2} \left[\sum_{n_2 \neq n_1} P_{n_2(A) n_1(A)} \, Baj_{n_1(A) n_2(A)} + \sum_{B \neq A} \sum_{n_1} P_{n_2(B) n_2(B)} \, Baj_{n_1(A) n_2(B)} \right],$$

n_1 and n_2 run over Valence to Rydberg AO's. Valence to Rydberg type exchange integrals are expected less significant and thus discarded.

$$\underset{\substack{\mu \rightarrow n_1(A) \\ \nu \rightarrow n_2(B) \\ \text{[IMRNHI/S-224E]}}}{F_{\mu\nu}} = \underset{\substack{\mu \rightarrow n_1(A) \\ \nu \rightarrow n_2(B) \\ \text{[MRINDO/S]}}}{F_{\mu\nu}} + \frac{3}{2} P_{\mu\nu} \, Baj_{n_1(A) n_2(B)},$$

$$Baj_{n_1(A) n_2(B)} = \left\langle \begin{matrix} \mu^A \nu^B \\ n_1 n_2 \end{matrix} \middle/ \begin{matrix} \mu^A \nu^B \\ n_1 n_2 \end{matrix} \right\rangle.$$

Further refinement over method, mono and bi-hybrid integrals (BHI) are converted into exchange, repulsion and overlap integrals using generalized Joshi-Chhaya approximation inspired by valence shell Mulliken approximation [2] BEI are

$$\langle \mu^A \nu^B / \mu^A \nu^B \rangle = \frac{2\langle \mu^A \mu^A / \nu^B \nu^B \rangle}{S_{\mu\nu}\, S_{\mu\nu}} - \frac{1}{2}\left[\langle \mu^A \mu^A / \mu^A \mu^A \rangle - \langle \nu^B \nu^B / \nu^B \nu^B \rangle\right].$$

Mulliken approximation is

$$\langle \mu\nu / \lambda\delta \rangle = \frac{1}{4} S_{\mu\lambda}\, S_{\nu\delta}\left[\langle \mu\nu/\mu\nu \rangle + \langle \mu\delta/\mu\delta \rangle + \langle \lambda\nu/\lambda\nu \rangle + \langle \lambda\delta/\lambda\delta \rangle\right].$$

An example for conversion of BHI into BRI + BEI is

$$\underset{[\mathrm{BHI}]}{\langle \mu^A \nu^B / \mu^A \mu^B \rangle} = \frac{1}{2} S_{\mu^A \mu^A} S_{\nu^B \mu^B} \left[\underset{[\mathrm{BRI}]}{\langle \mu^A \mu^B / \mu^A \mu^B \rangle} + \underset{[\mathrm{BEI}]}{\langle \mu^A \nu^B / \mu^A \nu^B \rangle} \right].$$

Inclusion of MHI renames the method as IMRMHI/S-224E.

$$\underset{[\mathrm{IMRMHI/S\text{-}224E}]}{F_{\mu\mu}} = \underset{[\mathrm{IMRNHI/S\ 224E}]}{F_{\mu\mu}} + \frac{1}{2}\sqrt{PIN} \sum_{\nu}^{A\, n_1} P_{\mu\nu}\left[\langle \mu^A \nu^A / \mu^A \nu^A \rangle + \langle \mu^A \mu^A / \mu^A \mu^A \rangle\right]$$

$$\underset{[\mathrm{IMRMHI/S\text{-}224E}]}{F_{\mu\nu}} = \underset{[\mathrm{MRINDO/S\ 224E}]}{F_{\mu\nu}} + \frac{1}{4}\sqrt{PIN}\, P_{\mu\mu}\left[\langle \mu^A \mu^A / \mu^A \mu^A \rangle + \langle \mu^A \nu^A / \mu^A \nu^A \rangle\right]$$

$$+ \sum_{\lambda \neq \mu,\, \lambda \neq \nu}^{A,n_1} \left[\langle \mu\nu / \mu\nu \rangle \left\{ P_{\mu\nu}\left(\frac{3}{2}\sqrt{PIN} - \frac{3}{8} PIN\right) + P_{\lambda\lambda}\left(\frac{3}{4} PIN - \frac{1}{2}\sqrt{PIN}\right)\right\}\right.$$

$$\left. + \langle \mu\mu / \mu\mu \rangle \left\{ \frac{1}{4} PIN\, P_{\lambda\lambda} - \frac{1}{8} PIN\, P_{\mu\nu} \right\} \right].$$

The product of two overlap terms $PIN = S_{\mu\nu} S_{\delta\lambda}$ is characterised as a same centre overlap arbitrary constant. $PIN = 1.0$ for $l = 0$ spherical symmetry. Hybridised AO's polarization makes same centre overlapping negligible in favour of higher bond capacity.

The trend of overlapping according to hybridization can be presented as

$$SP > SP^2 > SP^3 >> P\,.$$

Effects of parameters like temperature, pressure, charge transfer, chemical reaction, external radiation, screening *etc.* may change "PIN" accordingly by changing polarization of AO's. Thus "PIN" is adopted as an arbitrary constant. Various values of PIN are used to study molecules.

$$\underset{[\mathrm{IMRIAI/S\ 224E}]}{F_{\mu\mu}} = \underset{[\mathrm{IMRMHI/S\ 2241}]}{F_{\mu\mu}} + \sum_{n_2 \neq n}^{A} P_{n_1(A) n_2(A)} \left[\frac{1}{2}\sqrt{PIN}\, S_{\mu\nu}\left(Baj_{n_1(A) n_2(A)} + \Gamma_{n_1(A) n_2(A)} \right) \right]$$

$$+ \sum_{B \neq A} \sum_{n_1}^{B} P_{n_1(B) n_2(B)} \left[\frac{1}{2}\sqrt{PIN}\, S_{\mu\nu}\left(Baj_{n_1(A) n_2(B)} + \Gamma_{n_1(A) n_2(B)} \right) \right].$$

Inclusion of BHI renames method as IMRIAI/S-224E. IAI stands for inclusion of all integrals.

$$F_{\substack{\mu\nu \\ \mu\to n_1(A) \\ \nu\neq\lambda\to n_2(B) \\ \text{[IMRIAI/S-224L]}}} = F_{\substack{\mu\nu \\ \mu\to n_1(A) \\ \nu\to n_2(A) \\ \text{[IMRMHI/S 224L]}}} + \sum_{B\neq A}\sum_{\substack{\lambda\neq\mu \\ \lambda\neq\nu}}^{B} P_{\mu\nu}\left[\sqrt{PIN}\,\{\langle\mu\nu/\mu\nu\rangle\}\right.$$

$$-\frac{1}{8}S_{\mu\nu}S_{\mu\nu}\{\langle\mu\mu/\mu\mu\rangle+2\langle\mu\nu/\mu\nu\rangle\}$$

$$+\sum_{B\neq A}\sum_{\substack{\lambda\neq\mu \\ \lambda\neq\nu}}^{B} P_{\nu\nu}\left[\frac{1}{4}S_{\mu\nu}\sqrt{PIN}\,\{\langle\nu\nu/\nu\nu\rangle+2\langle\mu\nu/\mu\nu\rangle\}\right.$$

$$\left.\left.-\frac{1}{8}\sqrt{PIN}S_{\mu\nu}\{2\langle\mu\nu/\mu\nu\rangle+\langle\nu\nu/\nu\nu\rangle\}\right]\right].$$

For fine touch to the method and to prevent intermingling of Rydberg and valence AO's as well as S and P type AO's, BEI and BRI are bifurcated into 16 sub parts. *i.e* for BEI valence – Rydberg status.

$$Baj_{AB} = Baj_{\substack{n_1(A)n_2(B) \\ v\ v}} + Baj_{\substack{n_1(A)n_2(B) \\ v\ R}} + Baj_{\substack{n_1(A)n_2(B) \\ R\ v}} + Baj_{\substack{n_1(A)n_2(B) \\ R\ R}}$$

Each part of bifurcated parts is rebifurcated as

$$Baj_{\substack{n_1(A)n_2(B) \\ v\ v}} = Baj_{\substack{n_1^{v}(A)n_2^{v}(B) \\ v\ v}} + Baj_{\substack{n_1^{v}(A)n_2^{p}(B) \\ v\ v}} + Baj_{\substack{n_1^{p}(A)n_2^{v}(B) \\ v\ v}} + Baj_{\substack{n_1^{p}(A)n_2^{p}(B) \\ v\ v}}.$$

Here, P_x ($l=1$), P_y ($l=1$), P_z ($l=1$) atomic orbitals are not further differentiated according to $m_l = 2l+1$. Otherwise 24 more intra-subparts should be introduced.

Finally, the 'KE', molecular exchange screening is employed inspiring atomic screening $X = e^{-kd^0}$, $K = 1/r$. $KE = \text{Exp}\,[-KS.R_{ab}]$, $KS = \frac{1}{r_1} + \frac{1}{r_2}$ R_{ab} is internuclear distance (IND) and r_1, r_2 are the atomic radii.

For convenience, insignificant mono and bicentric three orbitals and four orbitals interactions as well as multi centre interactions are neglected.

For further improvement over basic method one may introduce inclusion of mono differential overlap as

$$F_{\substack{\mu\nu \\ \mu\neq\nu\to n_1(A) \\ \text{[INDO]}}} = P_{\mu\nu}\left[\frac{3}{2}\langle\mu^A\nu^A/\mu^A\nu^A\rangle-\frac{1}{2}\langle\mu^A\mu^A/\nu^A\nu^A\rangle\right]$$

$$+\eta\sqrt{PIN}\left[I_{n_1(A)}+I_{n_2(A)}\right],\ \eta \text{ is bonding Parameter.}$$

General Joshi – Chhaya Model is

$$\left\langle \mu^A \nu^B / \lambda^A \delta^B \right\rangle = \frac{14.3986}{R_{ab}^n + \left\{ \frac{1}{2} \left\langle \mu^A \nu^A / \lambda^A \delta^A \right\rangle + \frac{1}{2} \left\langle \mu^B \nu^B / \lambda^B \delta^B \right\rangle \right\}} \frac{1}{\gamma_n} \text{ eV}.$$

$\lambda = \mu$ and $\delta = \nu$ turn it as BEI,

$\nu = \mu$ and $\lambda = \nu$, $\delta = \nu$ turn it as BRI.

3. Ground state

Ozone (C_{2v}) : The removal of non-bonding HOMO B_1 (π_η) at 12.77 eV is found better compared to MRINDO/S [3] and agreeable to MO calculation [4]. Forbidden IP at 18.01 eV in the grid spectrum is well predicted by present method. Table 1 shows remaining results.

Carbon dioxide (C_{2v}) : The first IP is calculated with less estimation % error compared to MRINDO/S. Secondly, removal of σMO is well predicted at 19.27 eV. compared to MRINDO/S 19.07 eV. The experimental result [5] is 19.40 eV. Table 1 shows results with % estimation error.

Table 1. IP's in eV

Molecule	Exptl ΔE	MRINDO/S-CI[e]			IMRINDO/S-224-CI[f]		
		ΔE	Sym	% error in estimation	ΔE	Sym	% error in estimation
O_3 (C_{2v})	12.52[a]	12.79	A_2 (π_η)	2.1565	12.77	B_1 (π_η)	1.9968
	13.50[a]	13.62	B_2 (σ_n)	0.8888	13.67	B_2 (σ_n)	1.2593
	17.00[a]	17.17	B_1 (π)	1.0000	17.21	B_1 (π)	1.2352
		17.96	A_1(σ)	–	18.01	A_1 (σ)	–
CO_2(C_{2v})	13.78[a]	12.41	B_2(σ_n)	9.9419	12.65	A_1 (σ_n)	8.2002
	17.59[a]	15.62	A_1(σ)	11.2000	15.84	A_1 (σ)	10.1760
	19.40[a]	19.07	B_2 (σ)	1.7000	19.27	A_1 (σ)	0.6700
C_3H_4O(C_{2v})	8.90[b]	9.20	A_2 (π)	3.3707	8.75	B_1 (π)	1.6853
	10.82[b]	11.04	B_1 (π)	2.0332	11.16	B_1 (π)	3.1423
	13.06[b]	12.09	B_2 (n)	2.8330	12.89	A_1 (σ_n)	1.3016
	13.80[b]	13.65	B_2 (σ)	1.0869	13.70	A_1 (σ)	0.7246
	14.40[b]	13.86	B_2 (σ)	3.7500	13.90	B_2 (σ)	3.4722
	15.20[b]	14.86	B_1 (π)	2.2368	14.87	B_1 (π)	2.1710
	17.50[b]	15.25	A_1 (σ)	12.8571	15.42	B_2 (σ)	11.8857

Molecule	ΔE Exptl	RINDO-CI[g]			IMRINDO/S-111-CI[h]		
		ΔE	Sym.	% error	ΔE	Sym	% error
1,1 $C_2H_2F_2$(C_{2v})	10.72[c]	11.78	B_1 (π)	9.8880	10.54	B_1 (π)	1.6790
Trans $C_2H_2F_2$ (C_s)	10.38[c]	11.60	A (π)	11.7533	10.53	A (π)	1.4450
cis $C_2H_2F_2$ (C_{2v})	10.43[c]	11.53	B_1 (π)	10.5465	10.52	B_1 (π)	0.8628

Table 1. (*Cont'd*)

Molecule	Exptl					IMRINDO/S-222-CI	
HCN (C_{2v})	13.91[d]	-	-	-	12.94	σ	6.9734
Molecule	Exptl					IMRINDO/S-444-CI	
HCN (C_{2v})	13.91[d]	-	-	-	13.81	σ	0.7189

a = Turner *et al* [5] b = J H D Eland [9]
c = Kuppermann *et al* [10] d = J D Morrison and A J C Nicholson [8]
e = R S Prasad and C P Roy [31] f = Joshi *et al* (1994) [11]
g = Joshi *et al* (1993) [12] h = Joshi *et al* (1992) [13]

Furan (C_{2v}) : Expected fine results of ground state are obtained for large molecules like furan. Because employed improvement over BRI is allowed to have prapogating improvization over large molecular frame work. Present BRI are computed with less repulsive potential compared to MRINDO/S. Thus all the occupied MO's are obtained with less stabilization in favour of improvization.

Difluoroethylenes : IMRINDO/S-111-CI method helps to get agreement with experimental results [6] about the IP's. It also helps to predict the fact that the most easily removed electron in all isomers is $C = C\ \pi$. Table 1 shows success of present work. Moreover, calculated second and third IP's are associated with σ MO's. It proves that the substitution of fluorine for hydrogen in planar molecules has much larger stabilizing effect on the σ MO's. This is due to so-called perfluoro effect [7].

Hydrogen cyanide (C_{2v}) : $nnn = 222$ and $nnn = 444$ choices are found better to agree with experimental result [8].

In the most of molecules, inter nuclear distances (IND) are changed due to effect of vibration, rotation, temperature, external radiation, pressure *etc*. To study the changes of spectral properties according to tiny changes of IND, method as a smooth attnueator, IND can be formulated using $n = 2$ to $n = 16$ versions of Joshi-Chhaya Model [13].

In the present study, HCN molecule is chosen because it is known to exit in comets and in the interstellar medium. HCN is also thought to be one of the small molecules in the earth primeval atmosphere and an important source of intermediate in the formation of biological important chemicals. Say, under pressure with traces of water and ammonia, HCN pentamerizes to adenine. Moreover, it can also act as a condensing agent for amino acid to give polypeptides.

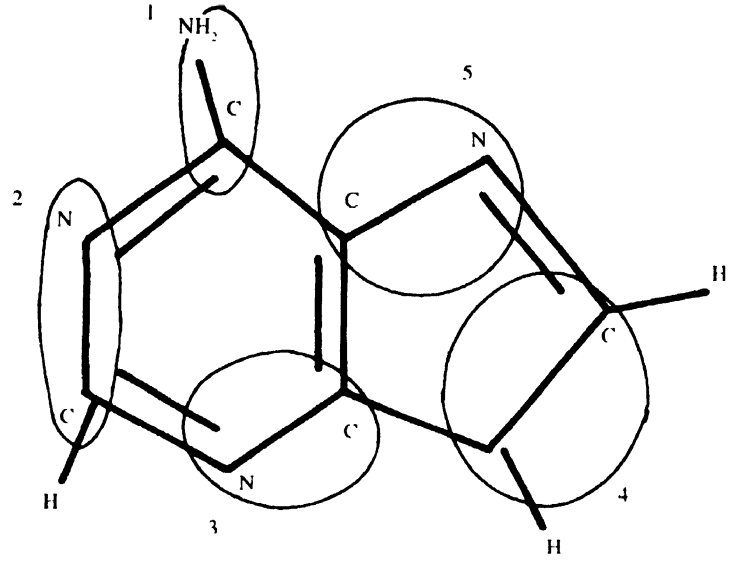
Figure 1 shows pentamerization of HCN into adenine incorporating two $\left[H-\overset{|}{\underset{|}{C}}-N\right]$ ions and three $\left[-\overset{|}{\underset{|}{C}}-N\right]$ ions of HCN.

Thus 40 % part of content is analogous to two successive removal of π electrons and σ MO holds high stability. 60 % part is due to first removal of σ electron following two π electrons.

$n = 1$ refers normal IND whereas $n = 2$ to $n = 16$ employ apparent reduction in IND and it can be assumed that the applied pressure indirectly a function of IND. Because extremely high pressure may change the IND.

Table 2 shows IP's of HCN at various values of n. $n = 2$ to $n = 7$ support 60 % content of HCN indicating first three successive removals of σ, π and π electrons respectively whereas $n = 9$ to 16 is in favour of 40% content of HCN predicting first two respective removals of π and

π electrons. At $n = 2$ to $n = 7$, HCN behaves traditionally by dissociating itself into H^+ and CN ions and indicates normal pressure. Thus automatically one may conclude that $n = 8$ to $n = 16$



1 Removal of H-C σ and C-N double π electrons
2 Removal of C-N double π electrons
3 Removal of H-C σ and C-N double π electrons
4 Removal of C-N double π electrons
5 Removal of H-C σ and C-N double π electrons

Figure 1. Structure of Adenine

are representing higher pressure and IND decreases gradually as pressure increases by changing n from 2 to 16. $n = 2$ to $n = 7$ results are providing 0.15 eV to 0.60 eV higher stabilization for $C \equiv N\pi$ MO's

i.e. $$E_{\pi} - E_{\sigma} = \Delta E_{\pi\sigma} = 0.15 \text{ to } .60 \text{ eV}$$

It causes σ MO to remove first. Second removal needs 0.15 to 0.60 eV More. Secondly both the $C \equiv N\pi$ MO's are found with almost equal energy.

i.e. $$E_{\pi_1} - E_{\pi_2} = \Delta E_{\pi_1\pi_2} = 0 \text{ eV}$$

It causes two C–N π electrons' removal at a time. IND and pressure according to $n = 7$ is found the most favourable to achieve the most stable $\left[-\overset{|}{\underset{|}{C}}-N\right]$ content by employing only 0.15 eV more after first removal. For the fourth removal of the same $\left[-\overset{|}{\underset{|}{C}}-N\right]$, approximately 9 eV more energy is required at $n = 7$. Suggesting highly stable electronic framework.

As per the expectation, at high pressure ($n = 09$ to $n = 16$), energies of first two highest occupied π MO's which were recognised as σ and π MO's at $n = 2$ to $n = 7$ calculation are computed with almost equal energies indicating trend to escape together. The third removal needs 0.22 to 0.46 eV more. Such a narrow gap between second and third IP's may cause

dissociation of HCN by absorbing little energy from external sources. This gap increases as n increases in favour to prevent short supply of 40 % content $\left[H-\overset{|}{\underset{|}{C}}-N\right]$ to pentamerization. To avoid third removal, high pressure is advisable upto somewhat less quantity compared to $\left[-\overset{|}{\underset{|}{C}}-N\right]$ σ bonding. This is the upper limit and $n = 8$ is lower limit of pressure. In the present case, the IMRINDO/S-nnn-CI method is convincing about why and how the pressure in terms of IND is needed for pentamerization. Pressure according to $n = 8$ is the key pressure requiring upward and downward smooth pressure gradient for healthy pentamerization. It also answers that why 100 % pentamerization is not achieved at intermediate pressure of ammonia. It may also predicts that why first living individual was not existed in the absence of high pressure.

Table 2. Five lowest ionization potential under IMRINDO/s-nnn-CI method of HCN ($C_{\infty v}$) in eV

n	Exptl ΔE	IP's									
		I		II		III		IV		V	
		Sym	ΔE	Sym	ΔE	Sym	ΔE	Sym	ΔE	Sym	ΔE
2	13.91[a]	σ	12.94	π_x	13.42	π_y	13.43	σ	21.87	σ	34.69
3		σ	13.42	π_y	14.03	π_x	14.03	σ	22.50	σ	35.18
4		σ	13.81	π_y	14.40	π_x	14.40	σ	22.98	σ	35.50
5		σ	14.19	π_x	14.67	π_x	14.67	σ	23.35	σ	35.76
6		σ	14.62	π_x	14.94	π_y	14.94	σ	23.82	σ	36.03
7		σ	15.04	π_x	15.19	π_y	15.19	σ	24.29	σ	36.28
8		π_x	15.42	σ	15.43	π_y	15.45	σ	24.72	σ	36.51
9		π_x	15.63	π_y	15.66	σ	15.78	σ	25.11	σ	36.71
10		π_x	15.80	π_y	15.84	σ	16.04	σ	25.43	σ	36.87
11		π_x	15.94	π_y	15.98	σ	16.26	σ	25.68	σ	37.00
12		π_x	16.05	π_y	16.10	σ	16.42	σ	25.89	σ	37.10
13		π_x	16.15	π_y	16.20	σ	16.57	σ	26.06	σ	37.19
14		π_x	16.23	π_y	16.28	σ	16.69	σ	26.24	σ	37.26
15		π_x	16.30	π_y	16.35	σ	16.79	σ	26.36	σ	37.32
16		π_x	16.35	π_y	16.40	σ	16.86	σ	26.47	σ	37.37

a = J D Morrison [8]

The present study is also helpful to predict that why highly efficient theoretical close coupling method based on variable finite IND parameter "a" calculates total cross sections with strange up and down under in the influence of finite dipole potential ? For HCN, the close coupling results [14] were found with one maximum cross section amount as the "a" changes. As a fact atleast one point on the potential surface with minimum potential should be formed to ensure stability of highly or weakly polar di atomic or poly atomic molecules.

In the present study of HCN, minimum energy point at $n = 3$, with $S \rightarrow S$ type excitation, anti parallel spin, $\Sigma 0 \rightarrow 0$ type transition, two "Z" directed Mo's, eigen vectors parallel to the

$H-C\equiv N$ molecular Symmetry axes, is found to ensure about molecular stability. Similar potential minimum points are found for

$$\pi_1 \rightarrow \pi^*_1, \pi_1 \rightarrow \pi^*_1, \pi_1 \rightarrow \pi^*_{1_R}, \sigma-\sigma^*, \sigma-\sigma^*_R \quad etc.....$$

For electron molecule scattering problem, external unexpected impurities and forces cause changes in IND and operate experiment with purturbed IND instead of predetermined normal IND. Thus theoretical results using normal experimental input data may not be found in accord with experiment. To avoid such unexpected problems, present IMRINDO/S-nnn-CI is useful to set IND by matching theoretical results to the IND invarient experimental data.

Table 3 shows results of first IP's using various values of same centre overlap "PIN" and the dominant BEI. BEI and MHI are calculated using Joshi-Chhaya model and included in the repulsive potential terms but 16 M.B. RAM is not sufficient to store bifurcated repulsive integrals into 16 parts. Thus only BEI are contracted as general form of BEI. To check effect of change of BEI on spectral properties, BEI are evaluated and employed as orbitary constant.

Table 3. First ionization potential of cisdifluoroethylene (eV)

Arbitrary values		IP ΔE	Nos of HOMO	Lowest Unoccupied MO ΔE
BAJ	$PIN^{1/2}$			
0 0	0 0	11 42	12	0 200
0 5	0 0	11 96	13	0 014
1 0	0 0	12 50	14	1 100
1 0	e^{-4}	12 53	14	1 04
1 0	e^{-5}	12 16	14	1 08
0 5	e^{-4}	11 99	14	1 71
0 5	e^{-5}	11 97	13	0 002
0 0	e^{-4}	11 45	12	0 2050
0 0	e^{-5}	11 43	12	0 226
0 0	e^{-2}	12 59	14	0 410

BHI are tested involving into potential terms and discarded to have more space in 16 M.B. RAM. Because of high screening and negligible mono centre overlap, results are found invariant. Results cited in Table 3 predict that inclusion of BEI and MHI causes high stability of all MO's. Occupied MO's are found with high degree of stability which may force the virtual MO's to plung below into negative energy region. Negligible value of the arbitrary constant "PIN" makes hybrid integrals insignificant. BEI are dominating over MO's stability. But proper weightage to MO's respect to quantum Nos. n and l as well as Rydberg intravalence and valence excitation, can be achieved by bifurcation of interaction integrals. Bifurcation helps to predict all the spectral properties reasonably.

4. Excited states

Table 4 and 5 show the encouraging results using improved theoretical SCF-LCAO-MO-CI method. Most of the results about spectral properties like S → S, S → T valence and Rydberg excitations are satisfactory obtained with less % error in estimation. Present reduced BRI

Table 4. Spectral properties in eV

Molecule	Exptl[a] ΔE	MRINDO/S-CI[c], s → s			IMRINDO/S-224-CI[b], s → s		
		Sym	ΔE	% error in estimation	Sym	ΔE	% error in estimation
O_3 (C_s)	1.24	A_2 ($\sigma_\eta \rightarrow \pi^*$)	1.04	16.12	A_2($\sigma_\eta \rightarrow \pi^*$)	1.03	16.94
	2.03	B_1 ($\sigma_\eta \rightarrow \pi^*$)	1.13	44.33	B_1 ($\sigma \rightarrow \pi^*$)	1.14	43.84
	3.72	B_2 ($\sigma_\eta \rightarrow \pi^*$)	3.57	4.03	A_1 ($\pi_\eta \rightarrow \pi^*$)	3.62	2.69
	4.86	B_1 ($\sigma \rightarrow \pi^*$)	5.08	4.53	B_1 ($\sigma \rightarrow \pi^*$)	4.98	2.47
CO_2 (C_{2v})	2.38	B_2 ($\sigma_\eta \rightarrow \sigma^*$)	1.93	18.90	B_2 ($\sigma_\eta \rightarrow \sigma^*$)	2.23	6.30
	3.54	A_2 ($\pi_\eta \rightarrow \sigma^*$)	2.06	41.80	A_2 ($\pi_\eta \rightarrow \pi^*$)	2.15	39.30
	6.53	B_2 ($\pi_\eta \rightarrow \pi^*$)	4.55	30.32	A_1 ($\pi_\eta \rightarrow \pi^*$)	4.68	28.33
	8.41	A_1 ($\sigma \rightarrow \sigma^*$)	5.06	39.83	B_2 ($\sigma \rightarrow \sigma^*$)	5.20	38.16
	9.31	A_2 ($\sigma \rightarrow \pi^*$)	6.51	30.10	A_2 ($\sigma \rightarrow \pi^*$)	6.65	28.57
	11.08	B_1 ($\sigma \rightarrow \pi^*$)	6.53	41.06	B_1 ($\sigma \rightarrow \pi^*$)	6.67	39.80

Molecule	Exptl ΔE	RINDO/S-CI[d]- s → s			IMRINDO/S-nnn-CI[b], s → s			
		Sym	ΔE	% error	Sym	nnn	ΔE	% error in
CHF=CHF	7.91[i]	$A_1(\pi \rightarrow \pi^*)$	8.34	15.99	A_1 ($\pi \rightarrow \pi^*$)	111	5.68	21.00
cis (C_{2v})	6.49[j]	$B_1(\pi \rightarrow \sigma_R^*)$	7.94	22.34	$A_2(\pi \rightarrow \sigma_{R_1}^*)$	111	7.56	16.49
	8.10[e]	$B_1(\pi \rightarrow \sigma_R^*)$	8.40	3.70	$A_2(\pi \rightarrow \sigma_{R_1}^*)$	111	8.05	0.62
	8.10[e]	$B_1(\pi \rightarrow \sigma_R^*)$	7.94	1.97	$B_1(\pi \rightarrow \sigma_R^*)$	222	8.24	1.72
CHH-CFF	7.19[i]	$A_1(\pi \rightarrow \pi^*)$	9.11	26.70	A_1 ($\pi \rightarrow \pi^*$)	111	5.87	18.36
(C_{2v})	6.95[h]	$B_1(\pi \rightarrow \sigma_R^*)$	8.60	23.74	$B_1(\pi \rightarrow \sigma_R^*)$	111	7.89	13.52
	8.10[g]	$B_1(\pi \rightarrow \sigma_R^*)$	9.24	14.07	$B_1(\pi \rightarrow \sigma_R^*)$	111	8.50	4.94
	8.10[e]	$A_1(\pi \rightarrow \pi_R^*)$	9.28	14.56	$A_1(\pi \rightarrow \pi_R^*)$	222	9.05	11.73
CHF-CHF	7.19[i]	A_1 ($\pi \rightarrow \pi^*$)	7.90	9.87	A ($\pi \rightarrow \pi^*$)	111	5.63	21.70
Trans (C_s)	6.64[g]	B ($\pi \rightarrow \sigma_R^*$)	9.06	36.45	B ($\pi \rightarrow \sigma_R^*$)	111	7.79	17.32
	8.10[g]	B ($\pi \rightarrow \sigma_R^*$)	9.06	11.85	B ($\pi \rightarrow \sigma_{R_1}^*$)	111	8.16	00.74
	8.10[g]	B ($\pi \rightarrow \sigma_R^*$)	9.16	13.09	B ($\pi \rightarrow \delta_R^*$)	222	8.95	10.49

Table 4. *(Cont'd)*

Isomer of Cisdifluoro ethylene	Exptl[a] ΔE $A_1(\pi\rightarrow\pi^*)$	RINDO-CI[d], S→T. ΔE(π→π*)	%error	IMRINDO/S-nnn-CI[e], S→T nnn	ΔE (π→π*)	% error
CIS	2 82	4 10	45.39	222	3 37	19 50
CIS	2 82	4 10	45 39	333	2 70	4 25
CIS	2 82	4 10	45.39	444	2 31	18.08
1,1	2 82	4 56	61 70	222	3 32	17 73
1,1	2 82	4 56	61 70	333	2 30	18 44
Trans	2 82	3.61	28 01	222	3.42	21 28
Trans	2 82	3.61	28 01	333	2 75	2 48
Trans	2 82	3 61	28 01	444	2 36	16 31

a = Turner *et al* [5] b = Joshi *et al* [11]
c = R S Prasad and C P Roy [3] d = Joshi *et al* [12]
e = Joshi *et al* [13] f = R M O'malley and K R Jenning [18]
g = M B Robin [19] h = Kuppermann *et al* [10]

compared to PP method [15-17] leads to increment in IND. Thus, all the MO's are treated with low stabilization. Total resiprocity is achieved including BEI and MHI.

Table 5. Spectral properties of cisdifluroethylene (C_{2v}) in eV

Method	IP ΔE	s→s π→π*	s→s $\pi\rightarrow\sigma^*_R$	s→s $\pi\rightarrow\sigma^*_R$	s→T $\pi\rightarrow\sigma^*_R$	s→T π→π* split	s→T π→π*	Average efficiency of method
IMRINDO/S-224 CI[a]	11 42	5 56	8 20	8 89	9 11	3 46	2 20	74 67
IRCNDO/S-224-CI[c]	12 02	5 35	8 69	8 92	9 52	2 87	2 48	75 49
IRINDO-224-CI[e]	11 64	7 01	8 38	8 76	9 07	2 30	4 71	83 80
IRINDO-224-CI[e]	12 29	7 03	8 86	9 15	9 74	2 02	5.01	77 48
IMRINDO/S-224E-CI[a]	11 16	5 77	8 11	8 82	9 02	3 75	2 02	73 78
IRCNDO/S-224E-CI[c]	11 77	5 45	8 55	8 83	9 45	3 13	2 32	74 80
IRINDO-224E-CI[e]	11 43	8.83	9 04	9 05	9 10	4 29	4.54	74 78
IRCNDO-224E-CI[e]	12 09	7.03	8 69	9 12	9 72	2 19	4 84	79 64
Exptl.[b,c,d]	10 72	7 19	6.49	6 49	8.10	2 82	4 37	100 00
RINDO[b]	11 53	8 34	7.94	8.40	9.03	4 10	4 24	80 69
MRINDO/S[f]	11.26	5 72	8.01	8 69	8 93	3.60	2 12	75 40

a = Joshi *et al* [11] b = M B Robin [19]
c = Kupermann *et al* [10] d = R M O'malley and K R Jenning [18]
e = Joshi *et al* [12] f = R S Prasad and A N Singh [20]

Spectral properties are almost depending on stability of MO's. In this screened method, π MO's are screened as

$$S_{\mu\nu} = KS_{\mu\nu} \text{ for } \pi \text{ MO's},$$

$K = 0.585$ for Valence interactions, 0.595 otherwise ; besides bonding screening is employed as

$$\beta^0_{n_1(A)n_2(B)} = n\left[In_1(A) + In_2(B)\right],$$

$n = 0.45$ for Valence resonance, 0.045 otherwise. More screening forces MO's to less sensible respect to changes like addition or neglect to integrals.

The expected trend of % sensitivity for attractive potential is

$$\sigma_u > \pi_u > \sigma_R > \pi_R$$

Thus, inclusion or neglect to attractive or repulsive potential terms in form of BEI, MHI, BHI *etc.* commands various MO's according to above given trend.

According our expectation, in the case of excitation of HCN, σ MO's get 5 eV stabilization whereas π_1 and π_1 MO's get 2.5 to 3.0 eV stabilization as n changes from 2 to 16. Moreover virtual π^*_1 and π^*_1 are found with only 1 eV stabilization.

To ensure stability of HCN molecule and to answer to scattering problem [14] $\sigma \rightarrow \sigma^*$ excitation energies are found with one minimum energy point at $n = 3$. A potential minimum point causes weak potential for $2s \rightarrow 3s$ transition allowing the incident electron for more penetration into target HCN dipole potential. A deep penetration of electron provides more time for electron-HCN interaction with multi centre scattering. As a result, total cross section amplitude at dipole range "a" = IND ($n = 3$) is obtained with high magnitude As "a" moves far from the IND at $n = 3$, both the sides, scattering amplitude falls down.

In favour of stability, $\pi_1 \rightarrow \pi^*_1$, $\pi_1 \rightarrow \pi^*_1$ and $\sigma \rightarrow \sigma^*_R$ excitation energies are calculated with atleast one minimum energy value at $n = 5$, $n = 7$ and $n = 3$ respectively.

$\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*_R$ both transitions are giving minimum energies at $n = 3$. Their respective lowest energies are calculated as 10.50 and 10.14 eV. Energy gap is found as 0.36 eV thus approximately 3.6 eV more energy is sufficient for incident electron to switch over valence excitation to Rydberg excitation. This leads to very low scattering amplitude due to high energy values of Rydberg $\sigma \rightarrow \sigma^*_R$ excitation at $n = 5$ to $n = 16$. This helps to get the best agreement with experimental results.

Finally, it can be concluded that addition in attractive potential is providing high stability for MO's. Inclusion of BEI and MHI are expected to predict real picture of molecular interactions.

Exchange integrals are responsible to give precise weightage to singlet – triplet splittings and excitations. BHI are found very less significant due to high screening. Bifurcation of BEI and BRI can prevent intermingling of *S* and *P* type atomic orbitals contributions and unexpected penetration of Rydberg part atomic orbital contribution to the valence interactions. In the attractive potential term mono-differential overlap should be retained.

The rational approach of all the additions and screenings may lead towards to formulate an effective theoretical method, which may open the doors of mysteries of nature.

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